

Bench-Scale Testing of Advanced Concepts for Direct Coal Liquefaction: Evaluation of Dispersed Mo Catalysts

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Introduction

The Advanced Concepts for Direct Liquefaction of Coal program was initiated by the U. S. Department of Energy in 1991 with the objective to develop process concepts that would reduce the cost of producing liquid fuels by the direct liquefaction of coal. Through investigating promising concepts through laboratory and bench-scale studies it is intended to develop sufficient technical and economic information to justify scale-up to a proof-of-concept operation. This paper presents the results from work performed under a contract awarded to the University of Kentucky to support a collaborative effort between the UK Center for Applied Energy Research (CAER), CONSOL, Inc. R&D, LDP Associates, Hydrocarbon Technologies, Inc. (HTI), and Sandia National Laboratories.

In Phase I of this project, which was completed in March 1995, a number of concepts were investigated on a laboratory scale, from which three were chosen for further investigation in continuous bench-scale runs in Phase II. When coupled, three of the concepts were shown to offer potential for improving direct coal liquefaction processing and reducing the cost of coal liquids. During the first continuous bench-scale run (ALC-1), which was made at HTI in the spring of 1996, two of the selected concepts were tested while operating in a slurry mode with dispersed catalysts.¹ In the first concept, Wyodak coal from the Black Thunder (BT) mine pretreated by low-pH oil agglomeration gave higher conversion (98%) than untreated coal (95%). In the second concept, recycle solvent was modified by dewaxing and hydrotreating. In this run a dispersed Fe-Mo catalyst was used which was a combination of HTI-proprietary ferrihydroxide hydrate (1 wt% Fe/dry coal)(FeOOH) and Molyvan A (MvA), which is N,N-dibutyldithiocarbamate of oxothiomolybdenum (100 mg Mo/kg dry coal) from Vanderbilt Chemical Co.

The second bench-scale run (ALC-2) was made at HTI during November-December, 1996 with the objective to test untreated Wyodak coal impregnated with water-soluble Mo-catalyst precursors in

combination with Fe and Ni precursors. By comparison with the base case run in ALC-1 with FeOOH-MvA, the relative activity of the impregnated catalysts could be determined relative to Mo introduced as an organically soluble precursor. Another objective was to determine the effect that co-addition of Fe had coal conversion, product distribution and unit operability. Other related objectives were to determine the necessity for uniformly dispersing the metal precursor onto the coal relative to impregnating it onto only a portion of the coal feed, i.e., 10%, and the effect of accumulated recycle catalyst concentration on process performance. An operating objective was to achieve maximum recycle of resid while producing a solids reject stream that was essentially equivalent to that produced by the ROSE unit operation at Wilsonville, i.e., with 75% solids content.

Selection of Catalysts

Since the activity achieved using a catalyst make-up rate of 100 mg Mo/kg dry coal was quite satisfactory, the target for ALC-2 was to determine whether the impregnated catalysts could operate at the same Mo addition rate, even though most laboratory results had indicated very little effect at a concentration of 100 mg Mo/kg coal. The incentive for targeting this concentration level was based upon catalyst cost. In Phase I, in the economics case that was developed based upon Wilsonville Run 262J, the total catalyst cost for this 2-stage process configuration was approximately \$3.50/bbl of gasoline product.² The nickel-moly 2nd-stage catalyst accounted for \$1.54 with the remaining cost was attributed to the 1 wt% Fe₂O₃ (\$0.74) and 100 ppm Mo added as Molyvan L (MvL, \$2.00). MvL is molybdenum di(2-ethylhexyl)phosphoro-dithioate in petroleum (8.1 wt% Mo) and is available from Vanderbilt Chemical. The impregnated catalysts are all based upon solubilizing MoO₃ directly in either ammonia, to give ammonium heptamolybdate (AM), or phosphoric acid, to give phosphomolybdic acid (PMA), and impregnating the solutions onto coal.³ This approach significantly reduces the cost of the catalyst. By using this approach the cost of the Mo catalyst would be \$0.31/bbl gasoline plus an additional 2-3¢ associated with the cost of ammonia or phosphoric acid. Surprisingly, the cost of using MoO₃ as precursor is less than the cost for the 1 wt% Fe₂O₃ in the base case, which provides an incentive to reduce or eliminate the Fe catalyst. However, because Fe addition at Wilsonville was reported to significantly improve operability, the approach taken in ALC-2 was to initially decrease Fe addition with the option of rapidly adding Fe as Fe-spiked coal to maintain operability, if necessary.

Economics, then, is a driving force for utilizing MoO₃ as the dispersed catalyst precursor. In the experimental work, *in lieu* of using MoO₃ and solubilizing it to impregnate the coal, AM and PMA were used directly both in the lab and at the pilot plant. Experimental results obtained at the CAER in microreactors showed that BT coal impregnated with AM gives both coal and resid conversions that are comparable to results with MvL (see Figure 1). AM in combination with Fe, which was impregnated as ferrous sulfate to a level of 0.18 wt% Fe on dry coal, also gave high THF conversion but resid conversion decreased. Ni, added as nickel sulfate at a concentration of 50 mg/kg dry coal, in combination with AM also gave high coal conversion along with high resid conversion. The addition of PMA at a level of 300 mg/kg dry coal also gave coal and resid conversion equivalent of MvA and MvL (see Figure 2). High coal and resid conversions were also observed for reaction of a coal mixture comprising 10% PMA impregnated coal and 90% untreated coal.

Bench-Scale Operation (ALC-2)

Preparation of Feed Coals

All of the coal feedstocks were prepared prior to the start of the run by spraying aqueous solutions of the precursor salts onto 136 kg (~300 lb) batches of pulverized BT coal that contained 9.7% moisture. Impregnation was carried out by placing the coal in a ribbon mixer to which dilute solutions of the individual metals were fed at a rate of ca. 1500 g/hr. To avoid any complications resulting from mixing the different metals and precipitation of insoluble salts, i.e., FeMoO_4 or NiMoO_4 , Ni was always added before Mo and Mo before Fe. The total amount of solution sprayed onto the coal increased the moisture content in the coal by ~2 wt%, which did not alter the coal handling properties. After addition of each 1500 g aliquot of salt solution the coal was agitated for one hour before adding another aliquot containing a second metal or removing the impregnated coal from the mixer. Eight samples of each batch were taken of which three were submitted for analysis. The impregnated coals were stored in plastic bags and sealed in plastic-lined barrels. Analyses of the impregnated coals are shown in Table 1.

Unit Configuration and Run Conditions

ALC-2 was carried out using a 25 kg/day bench-scale unit employing two equal-volume backmixed reactors with an interstage separator, as shown in Figure 3. The temperatures in the 1st and 2nd-stage reactors were a nominal 440 and 450 °C with a coal feed rate of 640 Kg/h·m³ to each reactor. Hydrogen was fed to the 1st and 2nd-stage reactors at a rate of 12 and 8 wt% on dry coal, respectively. H₂S at a concentration of 2 wt% sulfur on dry coal was added to the 1st-stage and ditertiary nonylpolysulfide (TNPS) was added to provide 0.5 wt% sulfur on dry coal to the 2nd stage. Pressure during the run was maintained at 17 MPa (2500 psig). The effluent from the 2nd-stage reactor was separated at high pressure into an overhead vapor stream that was fed directly to an online hydrotreater operated at 380 °C. The underflow was collected at reduced pressure and manually transferred to a continuous vacuum still (CVS) to provide a 427 °C (800 °F) cut. The overhead from the CVS was then passed to a continuous reduced pressure still (RPS) to give a 315 °C (600 °F) cut. During the first part of the run a fraction of the bottoms from the CVS was sent to a toluene extraction (TE) unit to remove solids. The RPS bottoms and the remaining CVS bottoms were returned to the slurry mix tank for recycle. After toluene extraction of CVS bottoms, the toluene soluble extract was recovered and returned to the slurry mix tank. The toluene insoluble extract was dried and sent to storage.

Because of difficulties in removing solids and their resulting accumulation in the recycle stream, toluene extraction was replaced by filtration after completing evaluation of the AM catalyst. The feed to the filter comprised a portion of the reduced pressure underflow from the high pressure separator. Filtrate was sent to the CVS and filter cake, after washing and drying, was sent to storage. Solids were effectively removed from the process stream for about one day after which it became apparent that they were passing through the filter media. After numerous attempts to modify the filter media to correct the problem, filtration was discontinued after completing evaluation of the Ni-AM catalyst. After that solids were removed by passing a portion of the CVS bottoms to an off-line batch vacuum still to generate a solids-rich 524 °C+ fraction for rejection.

Slurry Preparation and Composition

During ALC-2-1 through ALC-2-3, coal feed slurry was prepared by blending impregnated coal with

CVS and RPS bottoms plus TE oil, when available. During ALC-2-4, while solids were being rejected as 524 °C+ vacuum bottoms, vacuum still overhead was also recycled to the slurry feed tank *in lieu* of TE oil. During the course of the run the coal feed rate and the recycle slurry-coal ratio remained constant but the composition of the recycle slurry changed quite significantly as a result of the availability of CVS bottoms and TE oil (see Figure 4). The total solids in the feed stream, including coal, ranged upward from a target level of 45% to as high as 50% during the run due to the inability to effectively remove solids from the system. The corresponding concentration of metals in the recycle stream also varied, as shown in Table 2, to give a total Mo concentration that varied from 320 to 458 mg/kg dry coal feed. For some unexplained reason the concentration of Fe in the recycle stream never reached the background level of the Fe present in the feed coal. The concentration of Ni that was being added during ALC-2-3 appeared to increase rather rapidly, as expected, but failed to flush out of the system when PMA was added in ALC-2-4. Overall, the concentrations of the metals in the recycle stream appeared to correlate quite well with the ash concentration.

Conversion and Product Distributions

Because of poor ash recoveries, product distributions were calculated based upon a forced carbon balance. Yields of water, H₂S and NH₃ were then adjusted to achieve a balance for oxygen, sulfur and nitrogen, respectively. Hydrogen consumptions were taken as the difference between calculated hydrogen in the product and hydrogen in the feed. Coal conversion is based upon quinoline insolubles and ash measurements are reported on a SO₃-free basis. Net product distributions, as shown in Table 3, indicate that the average coal conversion for the four catalysts was 95.0±0.66%. The yield of C₂-C₃ gases in ALC-2 was higher by 4-6% than observed for FeOOH-MvA in ALC-1 Condition #1 while the consumption of H₂ was about the same. The 524 °C+ resid conversion ranged from a low of 79.8% for AM to a high of 90.3% for Ni-AM. The latter was close to that for FeOOH-MvA in ALC-1 (90.6%). The Ni-AM catalyst produced the highest C₄-524 °C distillate yield which was higher than for the AM and PMA catalysts by 13.7 and 10.3%, respectively. The amount of the heavier 343-524 °C cut in the distillate product was greater for the Ni-AM catalyst than for the others such that the actual C₄-343 °C yields were greater for the other three catalysts.

The wide variation in product distribution may be a reflection of the widely different compositions of the feed streams for each of the four catalysts. The wide variation in feed and product flow rates for each catalyst is shown in Figure 5, where the feed is separated into (1) the fraction of coal that readily solubilizes in the reaction, which is referred to as reactive coal, (2) recycled resid in the feed and (3) total 524 °C- product. Since the amount of coal in the feed stream was nearly constant, the variation in the products may have been due to fluctuations in the resid concentration in the feed. However, for the four impregnated catalysts, there is no linear correlation between the yield of the heavier 343-524 °C fraction in the product (also shown in Figure 5) and the resid concentration in the feed.

We may assume that for each catalyst the reactive coal and resid react at their own rates according to the following expression which represents their combined conversion to product.



Regression analysis of the data for the four catalysts in ALC-2 provides values of x and y of 0.74 and 0.39, respectively, with an R squared value of 0.98. This tight fit of the data suggests that the four catalysts in ALC-2 have the same activity for producing 524 °C- product and the Ni-AM catalyst

produces more heavy distillate than the other three catalysts. Including the data for FeOOH-MvA from ALC-1, the R squared value dropped significantly ($R^2=0.84$) indicating a reduced correlation. The latter may be a result of differences in run conditions between ALC-1 and ALC-2, though it has been recognized that the resid conversion for the FeOOH-MvA case was unusually high.

Solids Characteristics

The failure of toluene extraction and filtration to efficiently remove solids from the system was, in part, related to the passage of solids through the filter media. Subsequent studies at HTI in their TE unit showed that solids penetrated both a 2-micron cartridge filter as well as a 3-micron filter bag. Although in the laboratory it was found that solids would penetrate Whatman #41 paper (20-25 μm), they would not pass through Whatman #42 paper (2.5 μm). Neither optical nor electron microscopy could show any significant difference between ALC-1 HP-separator underflow samples, which were successfully filtered, and ALC-2 samples, which could not be filtered. In both cases, the solids were uniformly less than 2 microns in size, which suggests that they could easily go through the 15 μm filter paper that was used in both runs.

Conclusions

There were several quite successful aspects to ALC-2. First of all, the activity obtained with impregnated Mo catalysts was found to be comparable to the activity obtained with organically-soluble Mo precursors. The impregnation approach provides an opportunity to significantly reduce catalyst cost. It was also found that solubilization and coal and resid conversion to distillate products was the same for the four impregnated catalysts. Microautoclave experiments also showed that the catalysts gave about the same level of conversion. It was also found that adding Fe and Ni to the coal had no effect on either solubilization or conversion to distillate products and eliminating Fe did not affect the operability of the unit. In addition, the Ni-AM catalyst was found to have a higher selectivity for producing heavy distillate. The results suggest that not only can better results be obtained without the use of either Fe or Ni promoters, but catalyst cost can also be reduced.

Future Work

We are presently planning for the next run, and presumably final run under this program, which is scheduled for the Spring of 1998. The objectives of the run are to test the approach of impregnating the Mo catalysts onto only a portion (10%) of the feed coal and integrating this catalyst system with OA cleaned coal.

References

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Table 1. Metal Loadings for ALC-2 Impregnated Coals mg metal/kg dry coal					
	Batch No.	Mo	Ni	Fe	Moisture Wt%
ALC-2-1	L-902	106±1	3.3±0.8	3530±51	12.6±0.1
	L-903	97±5	3.5±0.3	3600±72	12.2±0.2
ALC-2-2	L-904	107±3	na	na	12.9±0.3
	L-905	110±3	na	na	11.3±0.2
ALC-2-3	L-906	92±1	51±1.6	1967±6	10.3±0.4
	L-907	91±1	51±0.2	1921±22	11.3±0.1
ALC-2-4	L910	93±2	3.2±0.4	2233±65	10.6±0.1
	L-911	93±4	4.1±0.2	2099±15	11.2±0.1
Vector	L-908	107±1	54±1	2196±42	9.0±0.2
	L-911	105±2	54±2	1894±33	9.4±0.2
Starting Coal	HTI 6213	0.0	4.0	1960	10.01

Table 2. Catalyst Concentration (mg metal/kg dry coal feed)					
	Back-ground	Fe-AM	AM	Ni-AM	PMA
Fresh feed rate					
Mo	none	97	110	94	93
Fe	1960	3600	1960	1960	1960
Ni	4	4	4	55	4
Recycle Solvent					
Mo		223	255	364	298
Fe		8780	7090	10380	8640
Ni		nm	nm	135	75
Recycle/Fresh					
Mo		2.3	2.3	4.0	3.2
Fe		2.4	3.6	5.3	4.4
Ni		---	---	2.5	---
ash		2.0	2.3	3.5	3.1

Table 3. Net Products from ALC-2					
	ALC-2-1	ALC-2-2	ALC-2-3	ALC-2-4	ALC-1-1
Catalyst	Fe-AM	AM	Ni-AM	PMA	FeOOH-MvA
Space velocity kg/hr*ft ³	623	663	650	660	683
Net Yields, w% maf coal					
C ₁ -C ₃	13.48	15.89	13.58	15.38	9.42
C ₄ -C ₇	7.65	6.77	6.80	6.43	4.95
IBP-177 C	13.27	11.00	11.94	11.74	13.65
177-260 C	16.34	11.16	8.57	11.56	11.29
260-343 C	18.64	16.79	16.27	17.10	23.34
343-454 C	2.29	1.73	19.00	4.67	14.60
454-524 C	1.58	2.98	1.59	2.33	1.21
524 C+	9.32	15.44	4.77	12.38	4.33
IOM	6.05	4.80	4.95	4.29	5.04
C ₄ -343 C	55.90	45.72	43.58	46.83	53.23
C ₄ -454 C	58.19	47.45	62.58	51.50	67.83
C ₄ -524 C	59.77	50.43	64.17	53.83	69.04
Water	13.36	13.91	15.78	14.54	13.83
Co _x	7.47	6.20	4.75	6.25	5.92
NH ₃ ,H ₂ S	1.04	0.76	1.04	0.86	-0.04
H ₂ Consumption	7.1	7.0	7.2	6.9	7.5
524 C+ Resid Conv	84.6	79.8	90.3	83.3	90.6

